

**Extended Abstract of Presentation for  
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**Photoemission experiments at SPring- Beamline BL25SU**

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A recent thrust in photoemission spectroscopy (PES) of solids is the use of photon energies in the soft x-ray range, say 300 eV and above into the kilovolt range. The primary motivation is to obtain increased bulk sensitivity, owing to the increased elastic escape depths for the higher kinetic energy photoelectrons that are thereby produced. Of course, such studies are not in principle new. PES using laboratory X-ray sources, e.g. Al K $\alpha$  with energy 1486.6 eV, has been performed for many years and early synchrotron studies using photon energies above 300 eV [1] are also documented in the literature. But typically the resolution that could be achieved for spectra with good signal to noise was not adequate or only marginal for addressing the physics issues of interest.

Increased bulk sensitivity is particularly important for correlated electron materials. The physics of such materials typically involves the rather localized d and f electrons of unfilled inner shells of transition metal, rare earth and actinide atoms. In solids the effects of Coulomb interactions among these electrons lead to large, interesting and often surprising departures from the behaviors expected within the traditional band theory of electrons in solids. Often the particular behavior observed is the result of a delicate balance between the scales of atomic orbital binding energies, various Coulomb energies and the kinetic energy of electron motion from site to site in the solid, i.e. the electronic bandwidth. Even small differences of one or another of these energies between the bulk and the surface of a solid can change the energy balance and produce an entirely different behavior for electrons near the surface and in the bulk. If one's goal [2] is to use PES spectroscopy to elucidate the electronic structures underlying the novel bulk properties of correlated electron materials, then one has a strong motivation to obtain spectra characteristic of the bulk.

A major circumstance leading to differences in electronic structure for the bulk and the surface is simply the reduced coordination number on the surface relative to the bulk, nominally a difference by a factor of two since half the crystal is missing on the surface. This difference then reduces the bandwidth, which may also lead to less effective screening of Coulomb interactions as well, with both effects tending to enhance the importance of the Coulomb interactions. Thus surfaces tend to be more strongly correlated than the bulk. One can also infer that additional reductions in coordination number for textured surfaces with, e.g., atoms at edges and sharp corners, will result in additional enhancements of such surface effects relative to those of atomically perfect surfaces. Theories [3] and experimental verifications [4] of particular versions of this scenario can be found in the literature.

The need to discriminate against the effects of surface texture in the pursuit of PES spectra characteristic of the bulk adds one more requirement beyond the use of higher photon energies, i.e. the need to limit the sample area probed to a region that is homogeneously untextured. One means whereby this can be accomplished is to have a small photon spot size.

A second advantage of higher photon energy soft X-ray PES is that one gains access to higher energy absorption edges, for which there is often a large resonance enhancement of the local orbital PES cross-section. The use of such cross-section resonances to separate and extract the local orbital spectrum is known as resonance photoemission spectroscopy (RESPES), an example being RESPES of the Ce 4f spectrum at the Ce 3d edge. The contrast between off and on resonance spectra for the higher energy absorption edges is typically much greater than for lower energy edges, e.g. the Ce 4d edge, simply because, in general, the PES cross-section at the higher photon energies is much less than at low photon energies. So, on the one hand, it is more challenging to obtain PES spectra with good signal to noise at higher photon energies, but on the other hand, the RESPES contrast is greater.

The first possibility for soft X-ray PES studies above 300 eV with both adequate resolution and signal to noise ratio came from experiments at beamline BL25SU at the SPring-8 synchrotron in Japan, conceived and constructed by S. Suga and his collaborators [5]. This beamline also produces a photon spot size that is nominally 0.1 mm in diameter. This Workshop presentation describes two studies done by the author and his collaborators, in collaboration with S. Suga and his group, at BL25SU.

One study is a measurement of the Ce 4f PES spectrum of the Kondo lattice compound  $\text{La}_{1-x}\text{Ce}_x\text{Al}_2$  for  $x$  reduced from 1.0 to 0.04 [6]. The purpose of the study is to test the so-called dense impurity ansatz for Ce materials with small Kondo temperatures. The essence of this ansatz is that the impurity Anderson model can provide a description of the angle integrated 4f spectrum of a concentrated Ce material, i.e. of the local properties of the 4f spectrum. The use of BL25SU has two advantages, bulk sensitivity and the capability for doing RESPES at the Ce 3d absorption edge to extract the 4f spectrum of the diluted sample. It is found that the spectra for  $x=0.04$  and  $x=1.0$  are nearly identical except for small differences in the near Fermi energy peak known as the Kondo resonance. These small differences are exactly as expected due to the known decrease of Kondo temperature with  $x$ , within the framework of the impurity Anderson model. Angle integrated 4f spectra for many large Kondo temperature Ce materials, obtained on beamline BL25SU by S. J. Oh and his collaborators [7], are also well described by the impurity Anderson model.

A second study led to the discovery [8] of a prominent quasi-particle peak in the V 3d PES spectrum of the paramagnetic metal (PM) phase of the Mott transition material  $\text{V}_2\text{O}_3$ . Such a peak is predicted by the so-called dynamic mean field theory (DMFT) of the Mott transition. DMFT is a lattice theory that can be formulated as an Anderson impurity model with a self-consistent “bath” of conduction electrons. This self-consistency leads to a description of the Mott transition in which a bootstrapped Kondo resonance appears in the correlation gap of the insulator for a critical value of the ratio of the bandwidth to the Coulomb energy. Previous studies of the PM phase of  $\text{V}_2\text{O}_3$  at low photon energy found at most a shoulder near the Fermi energy, quite inconsistent with the predicted peak. The combination of the high photon energy and the small spot available at beamline BL25SU was essential for avoiding surface contributions to the PES spectrum, these being from material that is more strongly correlated and hence has a much reduced Fermi energy peak. The new experimental result enables a comparison of theory and experiment that reveals that both the width and weight of the observed quasi-particle peak are greater than predicted by the DMFT theory.

These are but two examples of a number of important studies that have been made at beamline BL25SU. Although these examples both involve angle integrated PES, it is also possible to perform angle-resolved PES [9], which greatly enhances the scope of the potential of such studies. There is presently no similar capability for PES in the United States.

## References

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